ARTIFICIAL MATURATION OF COAL AND MACERAL CONCENTRATES: SATURATE AND POLYAROMATIC MOLECULAR MARKERS

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ABSTRACT

A sample from the "Simon" coal bed (Lorraine Basin, France) was separated into its constituent macerals vitrinite, exinite and inertinite by density gradient centrifugation. Aliquots of the macerals and whole coal were sealed in gold tubes with no added water and pyrolyzed separately at 350, 375, 400 and 450 °C for 24 hr at 100 MPa. The distributions of n-alkanes in the pyrolyzates are profoundly affected by pyrolysis temperature and sample type, but hopane and sterane distributions show little variation. The classic maturity parameters based on sterane isomerization are particularly ineffective. In contrast, distributions of polyaromatic hydrocarbons (PAH) change dramatically as a function of pyrolysis temperature. A variety of maturity-sensitive ratios are shown to be efficacious, including those employing dimethylphenanthrenes and methylpyrenes. These PAH ratios work particularly well for vitrinite pyrolyzates. For exinite pyrolyzates, the PAH ratios consistently show little change between 350 and 375°, but by 400° the ratios operate effectively.

INTRODUCTION

Slow, confined pyrolysis is often called upon for laboratory simulation of the thermal maturation of organic matter. The chief variables in confined pyrolysis experiments include temperature, duration of heating, the use of isolated kerogen vs. a kerogen/mineral mixture (natural or artificial), hydrous vs. anhydrous conditions, and the use of metal vs. glass reactors[1-7]. Confined pyrolysis provides a better simulation of natural petroleum generation in that its products lack the n-alkenes characteristic of open pyrolysis methods. While several studies have used open pyrolysis techniques in the characterization of isolated coal macerals[8-10], the present work is an attempt at confined pyrolysis of macerals, with the objective of observing of the effects of temperature and starting material type on distributions of saturate and, especially, aromatic hydrocarbons.

METHODS

The sample employed in the study is from the "Simon" coal bed (Lorraine Basin, France), petrographically determined to be 74% vitrinite, 13.2% inertinite, 5.5% exinite and 7.3% mineral matter[11]. Maceral separation by density gradient centrifugation[12] was performed on hand-picked lithotype concentrates. The resulting isolated macerals were vitrinite, inertinite (predominantly semifusinite and fusinite), and exinite (mainly sporinite and resinite). The pyrolytic and liquid chromatographic techniques used in this study have been previously described[11,13]. In brief, isothermal confined pyrolysis experiments in sealed, thin-walled gold tubes were run on 150 mg aliquots of the raw coal and of each of the three isolated macerals at temperatures of 350, 375, 400 and 450 °C for 24 hours at 100 MPa. The saturate and aromatic fractions of the pyrolyzates were analyzed by a Hewlett Packard 5890A gas chromatograph, coupled to an HP 5970B Mass Selective Detector (GCMS). The GC was held

initially at 100° C for 10 min., then raised to 300° at 3°/min., where it was held for 21 min. (saturates) or 5 minutes (aromatics). A 25 m OV-1 column with 0.2 mm inside diameter and 0.33 μm film thickness was employed. The mass spectrometer, using an ionization energy of 70 eV, was run in selective ion monitoring mode, collecting data on the principal fragment ions of biological marker compounds and on the molecular ions of the polyaromatic compounds.

RESULTS AND DISCUSSION

The normal alkane distributions vary considerably as a function of starting material and pyrolysis temperature. The 350° pyrolyzate of the whole coal shows a broad maximum in the C_{22} to C_{27} region, with a slight odd carbon number preference. There is a increasingly severe depletion of higher molecular weight n-alkanes as one progresses to the 375° and on to the 400° runs. The n-alkane concentrations in the 450° pyrolyzate are extremely low. The exinite n-alkane distributions for both the 350 and 375° runs are essentially the same and are very similar to the 350° whole coal run, except that they lack the odd carbon number preference. By 400° however, the exinite pyrolyzate shows a marked shift towards lower carbon numbers, roughly comparable to the 375° coal. Normal alkane distributions in the 350 and 375° vitrinites are also very similar to one another, having a maximum at C_{19}. They bear a strong resemblance to the 375° coal. By 400°, the overall concentration of n-alkanes decreases. The n-alkane distributions in the 350 and 375° inertinite pyrolyzates are very similar to one another, with a maximum at C_{21} and a slight odd carbon predominance. When compared to other samples, they most closely resemble the 400° vitrinite. The high temperature destruction of n-alkanes sets in at 400° for the inertinite. The yields of the 450° inertinite experiment were too low for analysis. Overall, there is a loss of higher molecular weight n-alkanes as pyrolysis temperatures increase. As higher temperatures ($\geq$ 400°) are reached, general destruction of n-alkanes occurs. 400° exinite resembles 375° coal and vitrinite. In turn, 400° vitrinite bears similarities to 350 and 375° inertinites. Thus, those samples richer in pyrolyzable and extractable organic matter lag behind the leaner in thermal alteration effects.

The hopane distributions show little variation among the samples, either as a function of temperature or starting material type. Lack of difference in hopane distributions in pyrolyzates of the macerals from a single coal is expected, because their bacterial precursors would have inhabited all macerals in the freshly deposited peat[14]. The steranes are a relatively minor component of the pyrolyzate saturate fractions. The sterane distributions within one sample vary even less than those of the hopanes as a function of organic matter type and level of thermal alteration. Consequently, the standard sterane maturation parameters[15] are ineffective, with the partial exception of the C_{29} ($\alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$) ratio for exinite.

A wide variety of polyaromatic molecular marker compounds are readily detectable in the aromatic fractions of the pyrolyzates, by setting the GCMS to monitor their molecular ions, which are often the strongest peaks in their mass spectra. These compounds include homologues and isomers of naphthalene, phenanthrene, dibenzothiophene, pyrene, fluoranthene and chrysene, as well as several pentaaromatic hydrocarbons. The distributions of these compounds exhibit profound changes due to thermal alteration. Aromatic steroids are among the most frequently employed aromatic molecular markers[16]. However, in this study they are not discussed, as C_{26}-C_{28} triaromatic steroids were detected in only 4 samples and monoaromatics were not detected at all. For the sake of brevity, only two groups of compounds are covered in this paper — the dimethylphenanthrenes and methylpyrenes, along with their isomers. A fuller discussion will be presented elsewhere[17].

Figure 1a presents an example of a partial m/z 206 mass chromatogram showing the distribution of dimethylphenanthrenes, ethylphenanthrenes and dimethylanthracenes, identified and, for simplicity, labelled as peaks 206a through 206j. In figure 1b, the quantitation results from the m/z 206 data for each of the vitrinite and exinite experiments are presented.

Excluding the ethylphenanthrene and dimethylanthracene peaks 206a, b and e, it can be seen that dimethylphenanthrene peaks 206c and d increase with pyrolysis temperature, while peaks 206f, g, h and i decrease. This phenomenon is shown in ratio form (fig. 1c), in which the ratio increases smoothly with temperature for vitrinite. There is little increase in the exinite ratio between 350 and 375°, but by 400°, the exinite value has nearly overtaken the vitrinite. The exinite ratio shows little further increase at 450°. The behavior of this ratio is in strong contrast to the commonly employed methylphenanthrene index[18], which increases from 350 to 400° for these samples, but drops sharply by 450°. Similar dimethylphenanthrene ratios have previously been employed[19,20].

The data from the m/z 216 partial mass chromatograms, showing distributions of methylpyrenes and methylfluoranthenes, are presented in figure 2 in a fashion analogous to that of figure 1, except that specific isomer assignments were not possible, due to the lack of standards and published identifications. Peak 216b increases with pyrolysis temperature, while peaks 216e and f decrease markedly. The resulting ratio (fig. 2c) increases nicely for vitrinite over the entire 350 to 450° temperature range. In contrast, the increase in the exinite ratio is delayed until temperatures climb above 375°, giving a curve very similar to the dimethylphenanthrene ratio (fig. 1c). Methylpyrenes have been previously used as thermal alteration indicators, but employing Shpol'skii spectral data, rather than GCMS[21].

Among the differences between vitrinite and exinite, the most profound is the delay in maturation response of the exinite between 350 and 375°, corresponding to the temperatures at which it is generating the most pyrolyzate[11]. This phenomenon is consistently detected by both Rock Eval and molecular parameters. The recognition of maturity-independent molecular characteristics is also desirable, but difficult in this case, since the range of thermal alteration levels is so great, and the effects of temperature so all-pervasive. However, some success may be expected in differentiating exinite and vitrinite, since their macromolecular structures are so dissimilar. Very little difference is apparent among saturate biomarkers, either due to maturity or organic matter type. For polyaromatic compounds, subtle features which differentiate the vitrinite and exinite pyrolyzates are worthy of note. Peak 206h (1,7-dimethylphenanthrene, also known as pimanthrene) appears relatively stronger in vitrinite (fig. 1b). Among methylpyrenes and methylfluoranthenes, peak 216c is also stronger in exinite than in vitrinite pyrolyzates (fig. 2b). Peaks 206h and 216c are minor features on their respective mass chromatograms and the differences tend to be lost by 450°. It would be of interest to examine a greater variety of maceral types from other coals and kerogens by the same methods, to determine if PAH distributions have greater potential for organic matter type differentiation than is apparent in this study.

CONCLUSIONS

1) The distributions of n-alkanes in the pyrolyzates are profoundly affected by pyrolysis temperature and sample type, but hopane and sterane distributions show little variation. The classic maturity parameters based on sterane isomerization are particularly ineffective.
2) Distributions of polyaromatic hydrocarbons change dramatically as a function of pyrolysis temperature. A variety of maturity-sensitive ratios are shown to be efficacious, including those employing dimethylphenanthrenes and methylpyrenes.
3) The aromatic ratios work particularly well for vitrinite pyrolyzates. For exinite pyrolyzates, these ratios consistently show little change between 350 and 375°, but by 400° the ratios operate effectively. For exinite, 350-375° is also the temperature range in which maximum generation of pyrolyzate occurs.
4) Vitrinite and exinite may be distinguished by subtle, temperature-independent features among the aromatic data.

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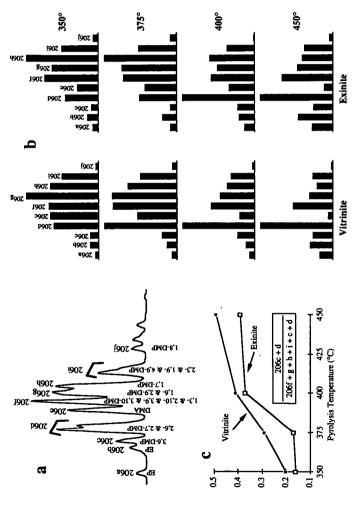
Figure 1 — Data from m/z 206 mass chromatograms of pyrolyzate aromatic fractions. 1a) Example of mass chromatogram (375° vitrinite). DMP peak identifications after Budzinski et al.[22]. EP: ethylphenanthrene, DMA: dimethylanthracene, DMP: dimethylphenanthrene. 1b) Peak distributions as a function of pyrolysis temperature and maceral type. 1c) Dimethyl-phenanthrene isomer ratio showing effects of thermal alteration.
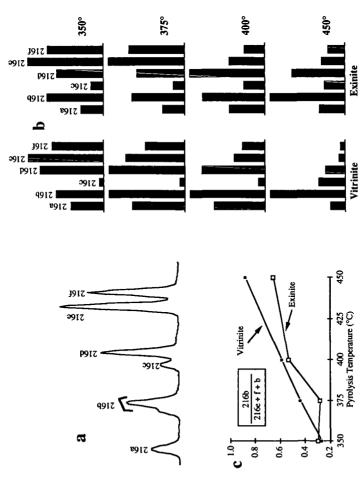
Figure 2 — Data from m/z 216 mass chromatograms of pyrolyzate aromatic fractions. 2a) Example of mass chromatogram (375° exinite), showing methylpyrene and methylfluoranthene isomers. 2b) Peak distributions as a function of pyrolysis temperature and maceral type. 2c) Isomer ratio showing effects of thermal alteration.